



# Biodiesel production from soybean oil in subcritical methanol using $\text{MnCO}_3/\text{ZnO}$ as catalyst

Liang Wan<sup>a</sup>, Hui Liu<sup>a,\*</sup>, Dejan Skala<sup>b</sup>

<sup>a</sup> State Key Laboratory of Biogeology and Environmental Geology and School of Environmental studies, China University of Geosciences, Wuhan 430074, PR China

<sup>b</sup> University of Belgrade, ICHTM, Center for Catalysis and Chemical Engineering, Belgrade 11000, Serbia



## ARTICLE INFO

### Article history:

Received 10 July 2013

Received in revised form 14 January 2014

Accepted 18 January 2014

Available online 27 January 2014

### Keywords:

Biodiesel

Solid base catalyst

Subcritical condition

Transesterification

Reusability

## ABSTRACT

The  $\text{MnCO}_3/\text{ZnO}$  catalyst with different Mn/Zn molar ratio were prepared using co-precipitation method and used for biodiesel synthesis in subcritical methanol. Prepared catalyst samples were characterized by basic strength, Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). The triglyceride (TG) conversion and fatty acid methyl ester (FAME) yield were determined using high performance liquid chromatography (HPLC). The effects of Mn/Zn molar ratio, calcination temperature and time, catalyst amount, molar ratio of methanol to oil, and transesterification reaction temperature and time, in regards to the catalyst activity were investigated. Results showed that a maximum TG conversion of 99.25% and FAME yield of 94.20% were obtained using  $\text{MnCO}_3/\text{ZnO}$  catalyst (Mn/Zn molar ratio of 1:1) calcined at 573 K for 0.5 h under such reaction conditions for biodiesel synthesis as 4 wt% of catalyst, methanol/oil molar ratio of 18:1, reaction temperature of 448 K, and reaction time of 1 h. The catalyst kept TG conversion above 91.54% and FAME yield above 86.26% after 17-cycle reuse in batch reaction without regeneration processes. Further reuse of catalyst is followed by deactivation mainly caused by the transformation of small particle ZnO to lamellate zinc glycerolate.

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## 1. Introduction

Due to the world-wide energy crisis, alternative renewable energy sources have recently attracted significant attention [1,2]. Biodiesel (fatty acid methyl esters), which derived from triglycerides (TG) by transesterification with methanol, is one of the attractive alternatives due to its renewability, biodegradability, and non-toxicity [3,4].

Commercially, biodiesel is mainly produced by the transesterification of vegetable oil using a homogeneous acid or basic catalyst, such as  $\text{H}_2\text{SO}_4$ , NaOH, or KOH [3,5,6]. However, in this process, catalyst removal and FAME, and glycerol purification is very difficult and a large amount of wastewater is simultaneously produced [7–10]. To solve this problem, a non-catalytic biodiesel production method with supercritical methanol has been developed [11,12]. However, this method requires extreme temperature and pressure conditions, e.g., 525–675 K and 35–60 MPa, and induces breakdown of unsaturated fatty acids and trans-isomerization, leading to adverse effects on the fluidity of the fuel at low temperature [13].

Furthermore, the synthesis of biodiesel in supercritical methanol requires a high investment cost for large scale industrial unit built as well as high energy consumption [14].

In order to improve the vegetable oil methanolysis and to decrease temperature and pressure and thus to reduce the energy consumption and avoid thermal degradation of triglycerides [15,16], many researchers attempted to add a small amount of solid catalysts or a co-solvent into the supercritical/subcritical methanol for biodiesel production [17–27]. For example, the supercritical transesterification in the presence of 3 wt% calcium oxide was essentially completed within 6 min at 525 K and with 41:1 methanol/oil molar ratio [17]. When the temperature was 533 K, the transesterification reaction was essentially completed within 10 min with 3 wt% nano-MgO and the methanol/oil molar ratio of 36:1 [18]. However, the reaction temperatures of these experiments were still very high ( $\geq 473$  K) and further energy consumption for biodiesel synthesis could be only obtained realizing synthesis at a lower temperature. For example, 9% CaO–CeO<sub>2</sub> catalyst was used at 383 K to catalyze the transesterification with 30:1 molar ratio of methanol to oil, however, the reaction time needed 5 h to get FAME yield of 91% [28]. Considering the economic benefit in industrial scale application, the stability and sustained activity of the catalyst is of important concern. Among many cases of different catalyst application, the nanoparticles of Zn/La showed desired

\* Corresponding author at: China University of Geoscience, No 388 Lumo Road, Wuhan, Hubei Province, China Tel.: +86 15927501778; fax: +86 27 87436235.

E-mail address: [zliuhui@hotmail.com](mailto:zliuhui@hotmail.com) (H. Liu).

activity and it was successfully reused for 17 times at 473 K [19]. Zinc aluminate doped with 5.5 wt% La (5.5% La/ZnAl<sub>2</sub>O<sub>4</sub>) exhibited high activity with biodiesel yield more than 95% after at 0.9 h at 437 K and 2.0 MPa. The deactivation and leaching of some elements of this catalyst, which was placed in fixed-bed reactor, was detected after 500 h of continuous operation [29]. However, Lanthanum, a rare element, is expensive and use of such catalyst will increase the cost of biodiesel production. Thus, it is of an interest to find cheaper and long life solid catalysts with high catalytic activities at lower reaction temperature, in shorter reaction time, and also lower molar ratio of methanol to oil.

For the purpose as above, solid MnCO<sub>3</sub>/ZnO catalysts were prepared with co-precipitation method for biodiesel production. The solid catalyst product before and after usage, as well as the individual Mn and Zn complexes, were characterized using different techniques and measurement: Hammett titration for determining the basic strength of catalyst, BET, SEM-EDS, XRD, FT-IR. Effects of the catalyst amount, Mn/Zn molar ratio used for catalyst synthesis, duration and temperature of calcination, molar ratio of methanol to oil, reaction temperature and time, on TG conversion were investigated to optimize catalyst preparation and transesterification conditions. The reusability of the solid catalyst was also investigated and the deactivation of the catalyst was discussed.

## 2. Experimental

### 2.1. Materials

Raw soybean oil was purchased from Baifu Oils & Fat Co. Limited (Wuhan, China). The physical–chemical properties of the soybean oil are listed in Table 1. Methanol and acetone of HPLC grade were purchased from Tedia Company Inc. (Fairfield, OH, USA) and Mallinckrodt Baker, Inc. (Phillipsburg, New Jersey, USA), respectively. The reagents K<sub>2</sub>CO<sub>3</sub> (99%), methanol (99.5%), ZnCl<sub>2</sub> (99%), MnCl<sub>2</sub> (99%) are of analytical grade, and were purchased from Aopu Chemical Company (Wuhan, China).

### 2.2. Catalyst preparation

The MnCO<sub>3</sub>/ZnO catalyst was prepared according to the co-precipitation method. K<sub>2</sub>CO<sub>3</sub> was used as a precipitant to deposit the mixed aqueous solution of MnCl<sub>2</sub> and ZnCl<sub>2</sub>. For a typical catalyst preparation, One hundred milliliter of aqueous solution containing 0.625 M MnCl<sub>2</sub> and ZnCl<sub>2</sub>, respectively, was slowly added into 600 mL 0.25 M K<sub>2</sub>CO<sub>3</sub> aqueous solution under vigorous stirring at 333 K. The catalysts with different Mn/Zn molar ratios were prepared by changing the molar concentrations of MnCl<sub>2</sub> and ZnCl<sub>2</sub> according but kept the total molar concentration of Mn and Zn at 1.25 M. The mixture was then aged at room temperature for 2 h. The solid product was recovered by filtration, followed

by thorough washing with deionized water and drying in an oven at 323 K overnight. The dried solid was calcined in a muffle furnace at various temperature (525–675 K) and time (0–24 h), and was stored in a desiccator. For comparison, two complexes, named Zn complex and Mn complex, using only ZnCl<sub>2</sub> and MnCl<sub>2</sub>, respectively, were also prepared using the same method as above and calcined at 573 K for 0.5 h.

### 2.3. Transesterification reaction

For catalytic tests a 500 mL stainless steel autoclave containing a stirrer, an internal cooling pipe, a temperature sensor, and an external heating jacket, was used (PCF0.5-10 JianBang Chemical Machinery Co. Limited, China). The maximum pressure and temperature of the autoclave are 10 MPa and 573 K, respectively. For a typical transesterification reaction, soybean oil, methanol, and catalyst were put into the autoclave and then heated to the pre-set temperature and stirred at a constant speed of 200 rpm. The reaction time was counted from when the temperature in autoclave reached the pre-set value at the controller. The pressure (1.8–3.2 MPa) of the reactor was measured by a pressure sensor. And after the expected reaction time, the transesterification of soybean oil was stopped by the tap water through the internal cooling pipe and water bath. Then, the autoclave was opened and the product was analyzed to determine triglycerides conversion.

### 2.4. Product analysis

Triglycerides (TG), Fatty acid methyl ester (FAME) and intermediate products, monoglycerides (MG) and diglycerides (DG), were analyzed using Agilent 1100 Series with a C18 column (40 °C, particle size 5 μm, 200 × 4.6 mm I.D.) and UV–Visible detection at 205 nm [30]. A linear gradient from 100% methanol to 50% methanol + 50% isopropanol–hexane (5:5, v/v) in 25 min was employed. The sample was diluted in HPLC grade acetone or isopropanol–hexane (1:50) and filtered through a 0.45 μm micropore membrane before analysis. TG conversion was calculated as the (percent) diminution of the sum of the areas of TG HPLC peaks. The FAME yield was calculated as the fraction (percent) of the sum of the areas of all FAME HPLC peaks relative to that of samples with maximum conversion.

### 2.5. Catalyst characterization

The basic strength of the samples (*H<sub>L</sub>*) was determined using Hammett indicator [31]. About 100 mg of the sample was shaken with 5 mL cyclohexane and 1 mL of Hammett indicators–benzene solution (0.1%, w/w) and then left to equilibrate for 2 h when no further color changes were observed. The Hammett indicators used and the corresponding *H<sub>L</sub>* values are as follows: 4-nitroaniline (*H<sub>L</sub>* = 18.4), 2, 4-dinitroaniline (*H<sub>L</sub>* = 15.0), phenolphthalein (*H<sub>L</sub>* = 9.8). The basic strength is defined as being stronger than the weakest indicator, which exhibits a color change, and weaker than the strongest indicator that showed no color change.

BET surface areas of the samples were determined according to the multipoint N<sub>2</sub> adsorption–desorption method using an instrument of SSA-4200 Surface Area & Pore Size Analyzer (Beijing Builder Electronic Technology Co., Ltd., China). Prior to measurements, all samples were out-gassed overnight under vacuum at 373 K.

XRD was performed on a D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. Cu Kα radiation (λ = 0.15418 nm), with a step size of 0.02° in the 2θ range from 5° to 65°, was used in all samples. The data were processed with the X'Pert HighScore Plus software. The peaks were identified using the Powder Diffraction File (PDF) database created by International Centre for Diffraction Data (ICDD).

**Table 1**  
Physical–chemical properties of the soybean oil used for the experiment.

Parameters	Values
Water content (wt%)	0.12
Acid value (mgKOH/g)	0.2
Density (g/cm <sup>3</sup> )	0.925
Saponification number	192
Fatty acid components (%)	
C16:0	16.5
C16:1	–
C18:0	2.0
C18:1	24.8
C18:2	51.8
C18:3	2.6
Others	0.6

FTIR spectra were recorded on a Nicolet FT-IR 5700 spectrometer (Thermo Electron Corporation, USA) over the wave number range of 4000–500  $\text{cm}^{-1}$ , with 2  $\text{cm}^{-1}$  resolution. The KBr pellet technique was applied for preparing samples. All measurements were conducted at room temperature.

Sample morphology and elemental chemical analysis at chosen points of samples were characterized at room temperature by a Quanta 200 SEM system equipped with EDS detector (FEI company, Netherlands). The accelerating voltage was 20 KV.

### 3. Results and discussion

#### 3.1. Optimization of catalyst preparation and transesterification reaction conditions

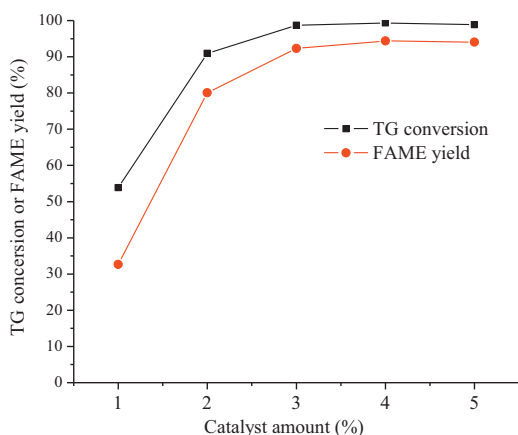
Following study was performed to optimize the catalyst preparation and transesterification reaction conditions, the effect of catalyst amount, Mn/Zn molar ratio, calcination time and temperature, methanol/oil molar ratio, transesterification reaction temperature and time, on the TG conversion and FAME yield were investigated.

##### 3.1.1. Catalyst amount

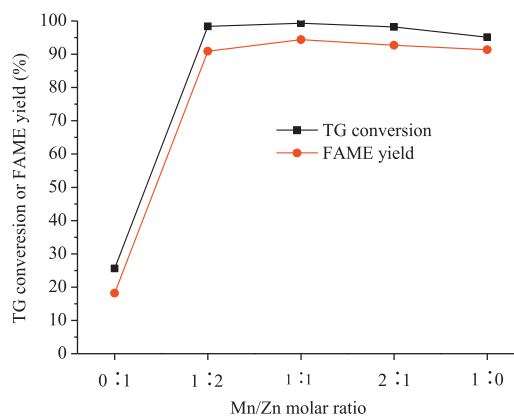
Catalyst amount is an important parameter which affects the conversion of triglycerides to methyl esters. Fig. 1 showed that the TG conversion evidently increased when the catalyst amount increased from 1% to 2%. A highest TG conversion of 99.35% with a FAME yield of 94.38% was obtained when catalyst amount was 4%, and no obvious increase was detected with further addition of catalyst. Generally, the increased usage of basic catalyst is favorable for the transesterification reaction [32]. However, disadvantage of increased amount of catalyst is that it raises the cost of biodiesel production. The experiment shows that the 4 wt% of catalyst is enough for this transesterification reaction.

##### 3.1.2. Mn/Zn molar ratio

The effect of Mn/Zn molar ratio on the activity of  $\text{MnCO}_3/\text{ZnO}$  catalyst was illustrated in Fig. 2. It showed that TG conversion and FAME yield were greatly dependent on Mn/Zn molar ratio. The Zn complex exhibited low activity with TG conversion of only 25.6% and FAME yield of 18.22%, and that activity of catalyst was remarkably enhanced by the addition of Mn. The highest transesterification efficiency was obtained for the catalyst prepared using Mn/Zn molar ratio of 1:1. Further increase of Mn/Zn molar ratio in prepared samples slightly decreased their activities. This



**Fig. 1.** Effect of catalyst amount on TG conversion and FAME yield. Catalyst  $\text{MnCO}_3/\text{ZnO}$  preparation conditions: calcination temperature = 673 K; calcination time = 24 h; Mn/Zn molar ratio = 1:1. Reaction conditions: molar ratio of methanol to oil = 36:1; reaction temperature = 448 K; reaction time = 1 h.



**Fig. 2.** Effect of Mn/Zn molar ratio on TG conversion and FAME yield. Catalyst preparation conditions: calcination temperature = 673 K; calcination time = 24 h. Reaction conditions: catalyst amount = 4%; molar ratio of methanol to oil = 36:1; reaction temperature = 448 K; reaction time = 1 h.

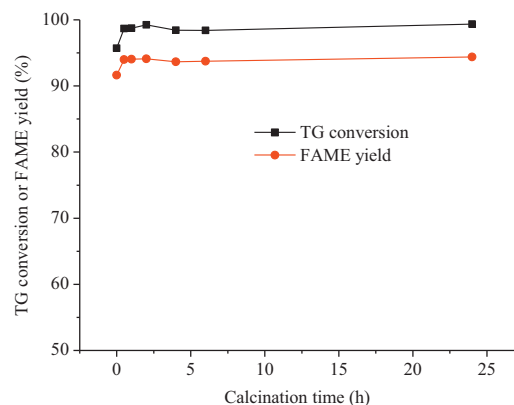
result suggested  $\text{MnCO}_3$  as main catalyst precursor, however, ZnO improve the activity of  $\text{MnCO}_3$ .

##### 3.1.3. Calcination time

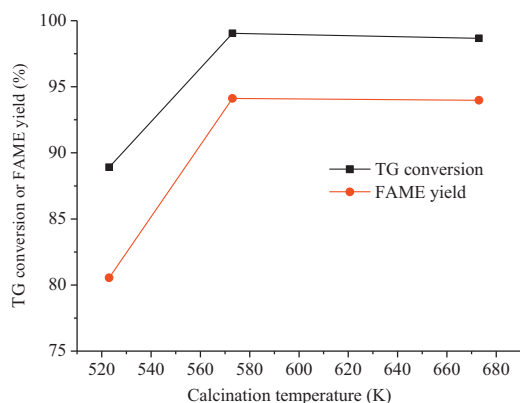
In order to investigate the effect of calcination time on transesterification efficiency and determine the optimal calcination condition for energy saving, a series of catalysts with various calcination times ranging from 0 to 24 h were prepared and used in the subcritical heterogeneous transesterification reaction. The results (Fig. 3) showed that even without calcination, high TG conversion (96.24%) and FAME yield (91.62%) were obtained. The TG conversion and FAME yield increased to 98.67% and 93.98%, respectively, when the catalyst was calcined for only 0.5 h. But longer calcination time didn't show further increase of catalyst activity. According to these results and taking into account energy consumption for catalyst preparation, the optimal calcination time of 0.5 h was selected to be the most appropriate.

##### 3.1.4. Calcination temperature

Effect of calcination temperature on the transesterification efficiency was presented in Fig. 4. It showed that, with the calcination temperature increased from 523 K to 573 K, TG conversion evidently increased from 88.9% to 99.04% while FAME yield increased from 80.55% to 94.12%. Transesterification efficiency with catalyst calcined at 673 K was the same as for the sample calcined at 573 K. Thus, the optimum calcination temperature was defined at 573 K.



**Fig. 3.** Effect of calcination time on TG conversion and FAME yield. Catalyst preparation conditions: calcination temperature = 673 K; Mn/Zn molar ratio = 1:1. Reaction conditions: catalyst amount = 4%; molar ratio of methanol to oil = 36:1; reaction temperature = 448 K; reaction time = 1 h.



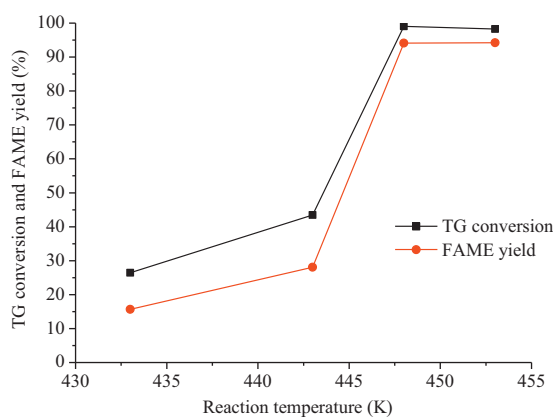
**Fig. 4.** Effect of calcination temperature on TG conversion and FAME yield. Catalyst preparation conditions: calcination time = 0.5 h; Mn/Zn molar ratio = 1:1. Reaction conditions: catalyst amount = 4%; molar ratio of methanol to oil = 36:1; reaction temperature = 448 K; reaction time = 1 h.

### 3.1.5. Transesterification reaction temperature

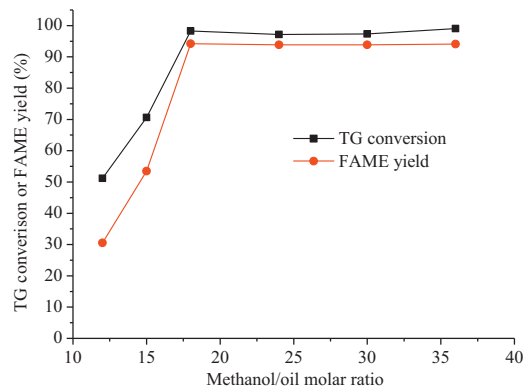
Temperature between 433 and 448 K on TG conversion and FAME yield were analyzed and obtained data presented in Fig. 5. It was found that TG conversion increased from 26.5% to 99.0% while FAME yield increased from 15.2% to 94.2% and for further testing of other parameters of biodiesel synthesis the optimal reaction temperature was set to be 448 K. The sudden increase of transesterification efficiency from 443 to 448 K may be caused by the physical state of methanol.

### 3.1.6. Methanol/oil molar ratio

The stoichiometric methanol/oil molar ratio required for the transesterification is 3:1. Due to the reversibility of reaction, a higher molar ratio is required to get desired conversion. However, increasing the alcohol amount beyond the optimal ratio will not increase the conversion, but will increase cost for excess alcohol recovery [33]. As shown in Fig. 6, TG conversion and FAME yield were only 51.2% and 30.6%, respectively, when low molar ratio of methanol/oil as 12:1 was used and further increases from 12:1 to 18:1 leads to higher TG conversion (98.3%) and FAME yield (94.2%). However, increasing of methanol/oil molar ratio above 18:1 showed very limited effect on TG conversion and FAME yield. Therefore, 18:1 is the appropriate methanol/oil molar ratio for this reaction.



**Fig. 5.** Effect of transesterification reaction temperature on TG conversion and FAME yield. Catalyst preparation conditions: calcination temperature = 573 K; calcination time = 0.5 h; Mn/Zn molar ratio = 1:1. Reaction conditions: catalyst amount = 4%; molar ratio of methanol to oil = 36:1; reaction time = 1 h.



**Fig. 6.** Effect of methanol/oil molar ratio on TG conversion and FAME yield. Catalyst preparation conditions: calcination temperature = 573 K; calcination time = 30 min; Mn/Zn molar ratio = 1:1. Reaction conditions: catalyst amount = 4%; reaction temperature = 448 K; reaction time = 1 h.

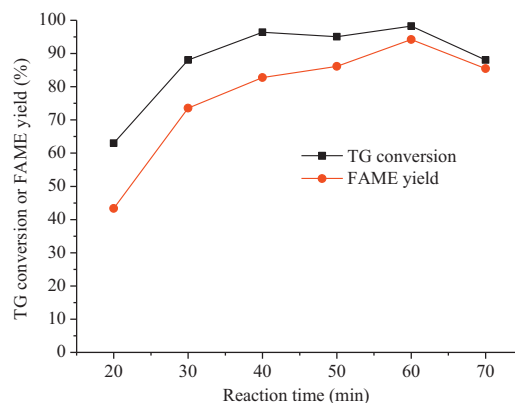
### 3.1.7. Reaction time

The reaction time also affects the transesterification efficiency of the process. Fig. 7 showed the effect of reaction time on subcritical heterogeneous transesterification. At the beginning of biodiesel synthesis the TG conversion and FAME yield increased rapidly with reaction time (from 20 to 40 min). The highest transesterification efficiency was reached after 60 min from the beginning of biodiesel synthesis. Thereafter, it started to decrease with the further increase of reaction time, which might be due to the reverse reaction between formed FAME (biodiesel) and glycerol [34].

In summary, the optimal catalyst preparation conditions have been determined as: Mn/Zn molar ratio is 1:1, calcination temperature is 573 K, and calcination time is 0.5 h. The optimal conditions for biodiesel production using the catalyst  $\text{MnCO}_3/\text{ZnO}$  are: 4% catalyst amount, methanol/oil molar ratio of 18:1, reaction temperature 448 K, and reaction time 60 min. Under these conditions, TG conversion reached 99.25% and the FAME yield was 94.20% accordingly. The HPLC chromatogram of the final product was illustrated in Fig. 8. There was very limited DG in the final biodiesel product, however, the amount of MG was considerable. Since MG was the most stable intermediate products, TG and DG were much easier esterified than MG [35].

### 3.2. Reusability of the catalyst

From economic point of view, the separation and reuse of catalyst in consecutive batches is of great importance for



**Fig. 7.** Effect of reaction time on TG conversion and FAME yield. Catalyst preparation conditions: calcination temperature = 573 K; calcination time = 30 min; Mn/Zn molar ratio = 1:1. Reaction conditions: catalyst amount = 4%; molar ratio of methanol to oil = 18:1; reaction temperature = 448 K.



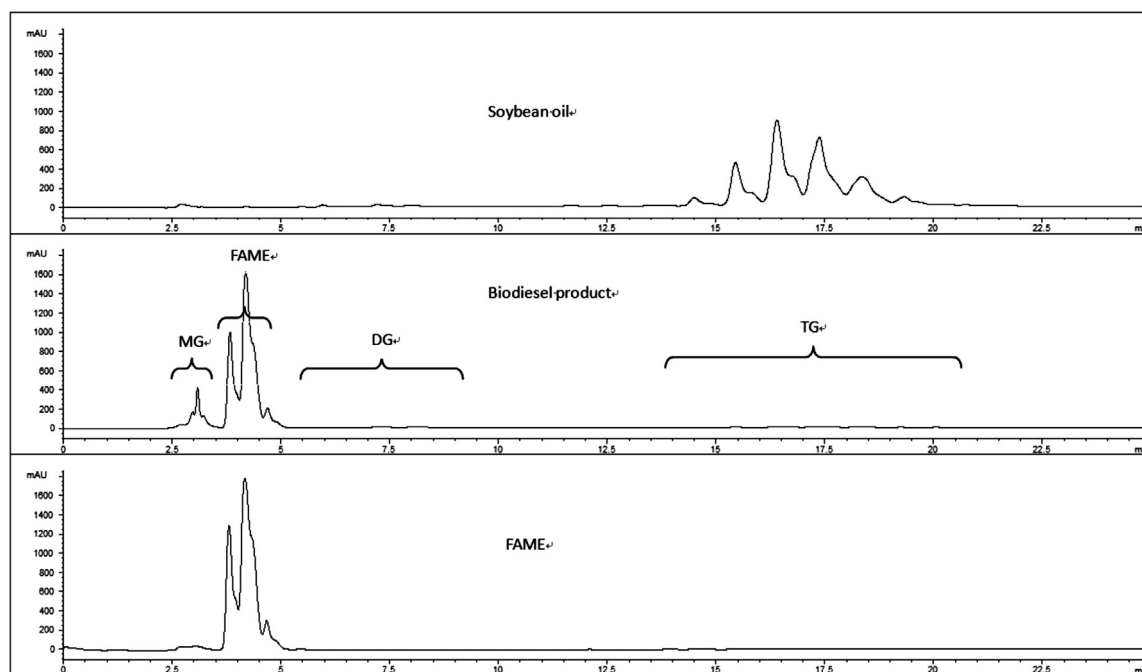


Fig. 8. HPLC chromatogram of soybean oil, final biodiesel product, and fatty acid methyl ester (FAME).

industrial application. After completion transesterification process, the reaction mixture was centrifuged and the catalyst was separated. Without any regeneration, the catalyst separated by centrifuge and remained in the reactor was reused in the next transesterification reaction directly. The results (Fig. 9) indicated that TG conversion and FAME yield kept above 91.54% and 86.26%, respectively, after 17 cycles of reaction followed by catalyst separation. Some decrease of TG conversion below 90% was observed after 18th cycle of reuse of the same amount of catalyst. The sustained activity of the catalyst will contribute in the lowering of the cost of biodiesel production on industrial scale.

### 3.3. Catalyst characterization

Fresh and reused  $\text{MnCO}_3/\text{ZnO}$  catalyst after 18 cycles, together with Mn and Zn complexes, were characterized by measuring the basic strength, BET surface area, XRD, FTIR, SEM-EDS, in order to understand the mechanism of catalyst activity and deactivation.

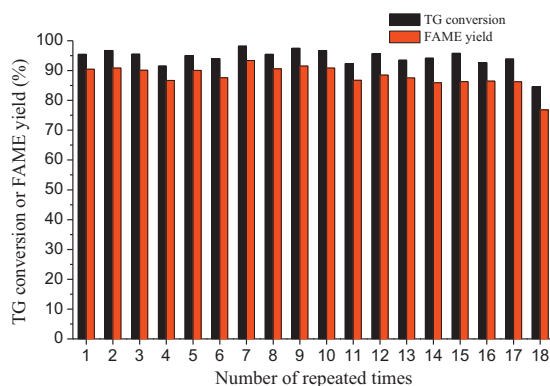


Fig. 9. Effect of repeated use of the catalyst on TG conversion and FAME yield. Catalyst preparation conditions: calcination temperature = 573 K; calcination time = 30 min; Mn/Zn molar ratio = 1:1. Reaction conditions: catalyst amount = 4%; molar ratio of methanol to oil = 18:1; reaction temperature = 448 K; reaction time = 1 h.

#### 3.3.1. Basic strength

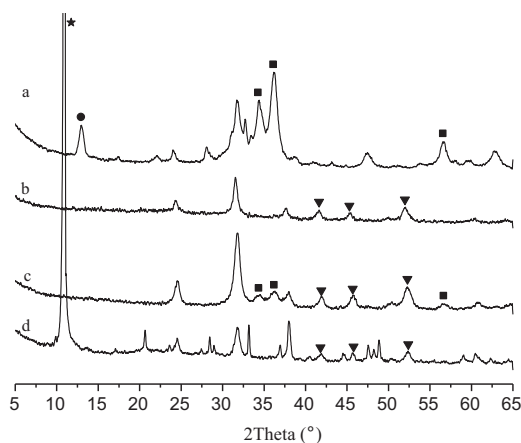
The catalyst  $\text{MnCO}_3/\text{ZnO}$  (molar ratio 1:1 of Mn/Zn) could change the color of phenolphthalein ( $H_- = 9.8$ ) from colorless to purple, but failed to convert 2, 4-dinitroaniline ( $H_- = 15.0$ ) from yellow to mauve, and therefore, its basic strength could be tentatively denoted as  $9.8 < H_- < 15$ . The basic strength of Zn complex was the same as that of the catalyst. However, Mn complex failed to convert the colorless phenolphthalein to purple, so its basic strength was  $H_- < 9.8$ . The basic strength of Zn complex is higher than Mn complex while Zn complex is much less active than Mn complex. Higher base strength is needed for the catalysis of transesterification reaction, but it is not that the higher, the better. The catalytic activity should also rely on other properties [31]. It is assumed that the basic strength of the catalyst higher than 9.8 is caused mainly by ZnO. The basic strength of the catalyst dropped from  $9.8 < H_- < 15$  to  $H_- < 9.8$  after being reused for 18 cycles. This result indicated that the presence of ZnO in the catalyst was changed during its repeated use.

#### 3.3.2. BET surface area

According to the multipoint  $\text{N}_2$  adsorption-desorption result, the BET surface area of the catalyst  $\text{MnCO}_3/\text{ZnO}$  (Mn/Zn molar ratio 1:1) is  $48.63 \text{ m}^2/\text{g}$ , while that of Zn and Mn complexes were  $44.49$  and  $70.02 \text{ m}^2/\text{g}$ , respectively. The 18 times reused catalyst exhibited almost 50 times lower surface area ( $1.06 \text{ m}^2/\text{g}$ ), which suggested that the physical structure of the catalyst was remarkably changed, too.

#### 3.3.3. X-ray diffraction (XRD)

X-ray diffraction patterns of the catalyst  $\text{MnCO}_3/\text{ZnO}$ , together with Zn and Mn complexes, were performed to determine the existing compounds of manganese and zinc in the catalyst. Fig. 10 have shown that the Zn complex had the typical diffraction peaks at  $2\theta = 13.0^\circ$  attributed to  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ , the precursor of ZnO [36]. It has been reported that the optimum decomposition temperature of  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  is 593 K [36]. So  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  was only partially decomposed to ZnO in the Zn complex (calcined at 573 K for 0.5 h). The fresh catalyst had the typical diffraction



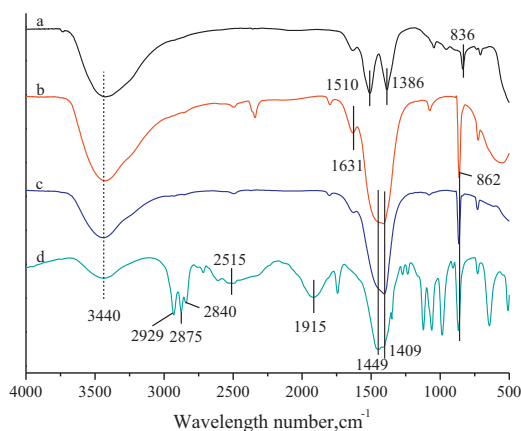
**Fig. 10.** X-ray diffraction patterns of Zn complex (a), Mn complex (b), fresh catalyst  $\text{MnCO}_3/\text{ZnO}$  with Mn/Zn molar ratio of 1:1 (c), calcined at 573 K for 0.5 h, and the catalyst after being reused for 18 cycles (d). (■), ZnO; (▼),  $\text{MnCO}_3$ ; (●),  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ ; (★),  $\text{C}_3\text{H}_6\text{O}_3\text{Zn}$ .

peaks at  $2\theta = 41.5^\circ$ ,  $45.3^\circ$ ,  $51.8^\circ$  and  $2\theta = 34.5^\circ$ ,  $36.3^\circ$ ,  $56.7^\circ$ , which were attributed to the crystals of  $\text{MnCO}_3$  and ZnO, respectively (according to the PDF of ICDD). No obvious peak of  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  was observed in the XRD pattern of the catalyst as  $\text{MnCO}_3$  was introduced. This implies that  $\text{MnCO}_3$  is accelerator of the catalytic  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  decomposition. Therefore,  $\text{MnCO}_3$  and ZnO were the dominant crystal forms in the prepared catalyst after calcination.

The XRD pattern of the used catalyst (Fig. 10) showed that a new crystal structure of zinc glycerolate was observed clearly at  $2\theta = 10.9^\circ$  [37], and the peaks of ZnO at  $2\theta = 34.5^\circ$ ,  $36.3^\circ$ ,  $56.7^\circ$  disappeared, which suggested that ZnO was transformed to zinc glycerolate in the biodiesel production process.  $\text{MnCO}_3$  was still in the catalyst after used because the peaks at  $2\theta = 41.5^\circ$ ,  $45.3^\circ$ ,  $51.8^\circ$  were remained.

### 3.3.4. Fourier transform infrared (FTIR) spectra

FTIR spectroscopy (Fig. 11) was used to investigate the functional groups of  $\text{MnCO}_3/\text{ZnO}$  catalyst, as well as Zn and Mn complexes. A broad band at around  $3440\text{ cm}^{-1}$  and other weak band at  $1631\text{ cm}^{-1}$  were attributed to O–H bands [37]. The band trend at around  $500\text{ cm}^{-1}$  was attributed to the vibration of Zn–O bond [38], and the peaks at  $1510\text{ cm}^{-1}$ ,  $1386\text{ cm}^{-1}$  and  $836\text{ cm}^{-1}$  are corresponding to the bending vibration of  $\text{CO}_3^{2-}$  in Zn complex (Fig. 11a) [39]. So  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  and ZnO should be the main composition



**Fig. 11.** FTIR spectra of Zn complex (a), Mn complex (b), fresh catalyst  $\text{MnCO}_3/\text{ZnO}$  with Mn/Zn molar ratio of 1:1 (c), calcined at 573 K for 0.5 h, and the catalyst after being reused for 18 cycles (d).

in Zn complex. The characteristic peaks at  $1449\text{ cm}^{-1}$ ,  $1409\text{ cm}^{-1}$ , and  $862\text{ cm}^{-1}$  (Fig. 11b) were assigned to  $\text{CO}_3^{2-}$  vibrations in Mn complex [40], which indicated that  $\text{MnCO}_3$  is the dominate compound in Mn complex.

The broad band at  $1449\text{ cm}^{-1}$ ,  $1409\text{ cm}^{-1}$ , and  $862\text{ cm}^{-1}$  in fresh catalyst (Fig. 11c) were similar to that of Mn complex, which indicated the existence of  $\text{MnCO}_3$  in the catalyst. On the other hand, the characteristic peaks of  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  at  $1510\text{ cm}^{-1}$  and  $1386\text{ cm}^{-1}$  disappeared, which indicates that  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  is not present in the catalyst. So  $\text{MnCO}_3$  and ZnO were the main constituent of the catalyst and this finding is consistent with XRD analysis.

FTIR spectrum of the used catalyst (Fig. 11d) showed that apart from the broad O–H bands (at  $3440\text{ cm}^{-1}$ ), the expected C–H bands (at  $2929$ ,  $2875$ ,  $2840\text{ cm}^{-1}$ ) and the reported other strong zinc glycerolate bands [41] were observed at  $2515$  (hydrogen bond between two oxygen atoms),  $1915$ ,  $1235$ ,  $1122$  (C–O stretch),  $1060$ ,  $985$ ,  $867$ ,  $644$ , and  $509\text{ cm}^{-1}$  [37]. The typical peak of  $\text{MnCO}_3$  at  $1449$  and  $1409\text{ cm}^{-1}$  did not change in the used catalyst. This analysis confirmed that ZnO in the catalyst had been transformed into zinc glycerolate, and  $\text{MnCO}_3$  did not change at all.

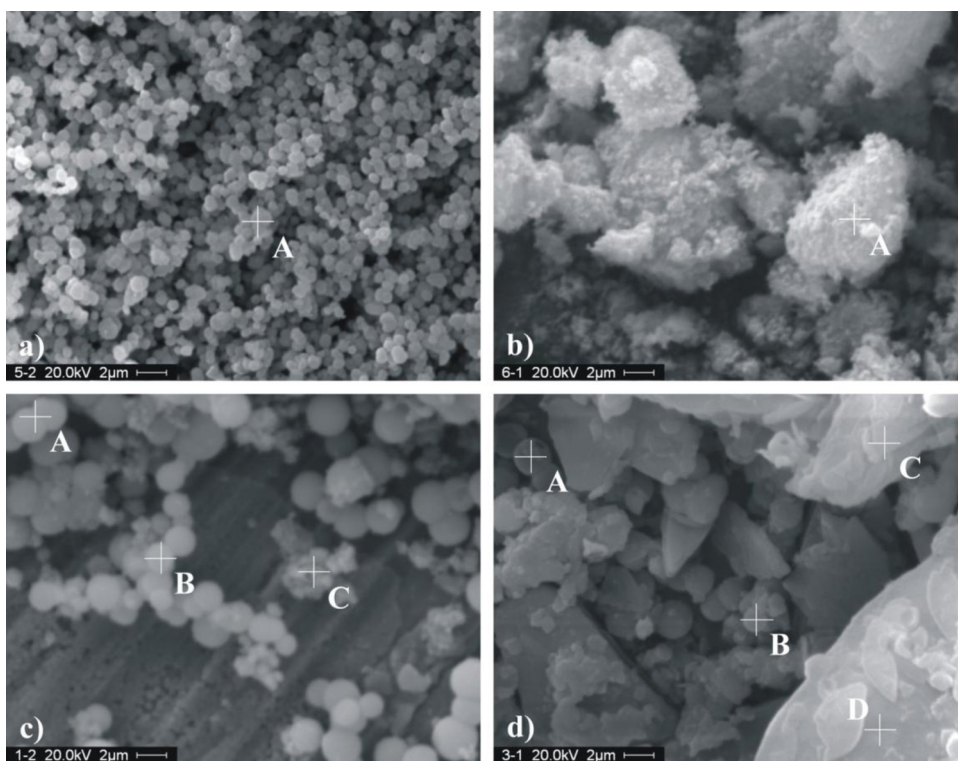
### 3.3.5. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS)

The SEM results showed that the Mn complex (Fig. 12a) was evenly distributed globular granules with diameters less than  $1\text{ }\mu\text{m}$ . The Zn complex (Fig. 12b) was caked micro particles. The fresh catalyst (Fig. 12c) was globular particle with smooth surface, whose size was about two times of that of Mn complex, which indicated the formation of new complex. Around the catalyst particles, some small granules were crystallized independently.

Several typical points on the surface of samples were selected for EDS analysis in order to determine the elemental contents of Mn, Zn, C, and O. Table 2 showed that at the points A and B of in Fig. 12c, the Mn/Zn ratio was about 1:1 that was equal to that of fresh  $\text{MnCO}_3/\text{ZnO}$  catalyst. The Mn/Zn molar ratio of the point C in Fig. 12c was much lower, which demonstrated that the small granules crystallized around the globular particles mainly consisted of ZnO.

The crystal morphology of the used catalyst (Fig. 12d) was very different from that of fresh catalyst. Instead of tiny particle of ZnO, new lamellate structure appeared around the globular particles, which could explain why the BET surface area of the catalyst after being reused decreased from  $48.63\text{ m}^2/\text{g}$  to  $1.06\text{ m}^2/\text{g}$ . EDS results (Table 2) showed that the Mn/Zn ratio of the new slice structure was much lower than that of the globular particles, which indicated that the new slice structure was formed mainly by Zn complex. The results of basic strength, BET surface area, XRD, and FTIR, confirms that the new formed slice is zinc glycerolate. So the deactivation of catalyst after reused for 18 cycles was mainly due to the transformation of small granule ZnO to lamellate zinc glycerolate.

Similar phenomenon of zinc glycerolate formation was observed when zinc carboxylate salts, zinc hydroxide acetate, and zinc hydroxide nitrate salts were used to catalyze soybean oil transesterification at  $100$  and  $140^\circ\text{C}$  [42]. This newly formed zinc glycerolate was proved to be able to convert soybean oil into fatty acid methyl esters with 66–76% yield and up to 95–97% TG conversion in the  $100$ – $140^\circ\text{C}$  reaction temperature range studied. And it showed a long life and could be reused for five catalytic cycles without deactivation or selectivity loss. On the other hand, it exhibited good tolerance toward  $0.5\text{ wt}\%$  water and  $10\text{ wt}\%$  fatty acids, without important decreases in the TG conversion. And after 2 h of consecutive uses, zinc was not detected in the polar and non-polar phases. Therefore, the newly formed zinc glycerolate is an effective catalyst for biodiesel production. However, in our experiment, the formation of zinc glycerolate from ZnO decreased the



**Fig. 12.** SEM of Mn complex (a), Zn complex (b), fresh catalyst  $\text{MnCO}_3/\text{ZnO}$  with Mn/Zn molar ratio of 1:1 (c), calcined at 573 K for 0.5 h, and the catalyst after being reused for 18 cycles (d).

**Table 2**  
EDS analysis of typical surface points in Fig. 12.

Pictures	Test point	Element contents (at%)			
		Mn	Zn	C	O
Fig. 12a	A	21.73	0	31.29	46.97
Fig. 12b	A	0	29.24	30.67	40.09
Fig. 12c	A	13.93	13.19	27.35	45.54
	B	10.08	12.02	30.19	47.71
	C	3.89	14.75	35.85	45.52
Fig. 12d	A	31.77	29.74	32.22	6.27
	B	22.61	24.45	41.82	11.12
	C	6.77	12.42	55.31	25.50
	D	5.78	12.26	55.70	26.26

catalyst activity. This may be mainly due to the sharp decrease of the surface area caused by the formation of slice structure from small granules. This structure changes is not acceptable if the catalyst is used in continuous fix-bed reactor, which will cause block of the reactor. However, it is suggested to grind the used catalyst to a particular size and then reuse it.

#### 4. Conclusion

Experiments performed in this study showed that the novel  $\text{MnCO}_3/\text{ZnO}$  catalyst sustained catalytic activity for biodiesel synthesis at 448 K. The TG conversion of the transesterification reaction catalyzed by  $\text{MnCO}_3/\text{ZnO}$  catalyst achieved 98.3% under the optimized catalyst preparation and transesterification reaction conditions: Mn/Zn molar ratio of 1:1, calcination temperature 573 K, calcination time 0.5 h, transesterification reaction temperature 448 K, 4% catalyst amount, 18:1 methanol/oil molar ratio, and 60 min transesterification reaction time. This catalyst was reused 17 times and has shown that the  $\text{MnCO}_3/\text{ZnO}$  catalyst could maintain a high catalytic activity without regeneration. Therefore, the  $\text{MnCO}_3/\text{ZnO}$  is a promising catalyst for the biodiesel production

in industry due to its stability, sustained activity, moderate calcination and reaction temperatures, and short time necessary for catalyst calcination as well as for biodiesel synthesis. The deactivation of the catalyst after 18th cycles of its reuse was caused by the transformation of small granule  $\text{ZnO}$  to lamellate zinc glycerolate.

#### Acknowledgements

This study was supported by the International S&T Cooperation Program of China (Grant No. 2013DFG92250), the “New Century Excellent Talent of Ministry of Education of China” project (Grant No. NCET-09-0713), and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan).

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